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Pollution Abatement in a Copper Wire Mill

Environmental Protection Agency, Cincinnati, Ohio

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3 EPA TECHNOLOGY TRANSFER CAPSULE REPORT

POLLUTION ABATEMENT IN A COPPER WIRE MILL

U.S. ENVIRONMENTAL PROTECTION AGENCY INDUSTRIAL DEMONSTRATION GRANT WITH VOLCO BRASS & COPPER COMPANY

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This Capsule Report shows how water consumption in copper wire mills can be reduced by 90%. The reduction was from 200,000 gallons per day to 20,000 gallons per day by chemical rinsing and water reuse. The sulfuric acid pickle was regenerated and high purity metallic copper recovered by continuous electrolysis, thereby, eliminating the dumping of spent pickle liquor. This new process is currently being used at several installations manufacturing copper and copper-alloy products. The chemical rinse technique is applicable to electroplating operations and has gained wide acceptance there.

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16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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3 CAPSULE REPORT

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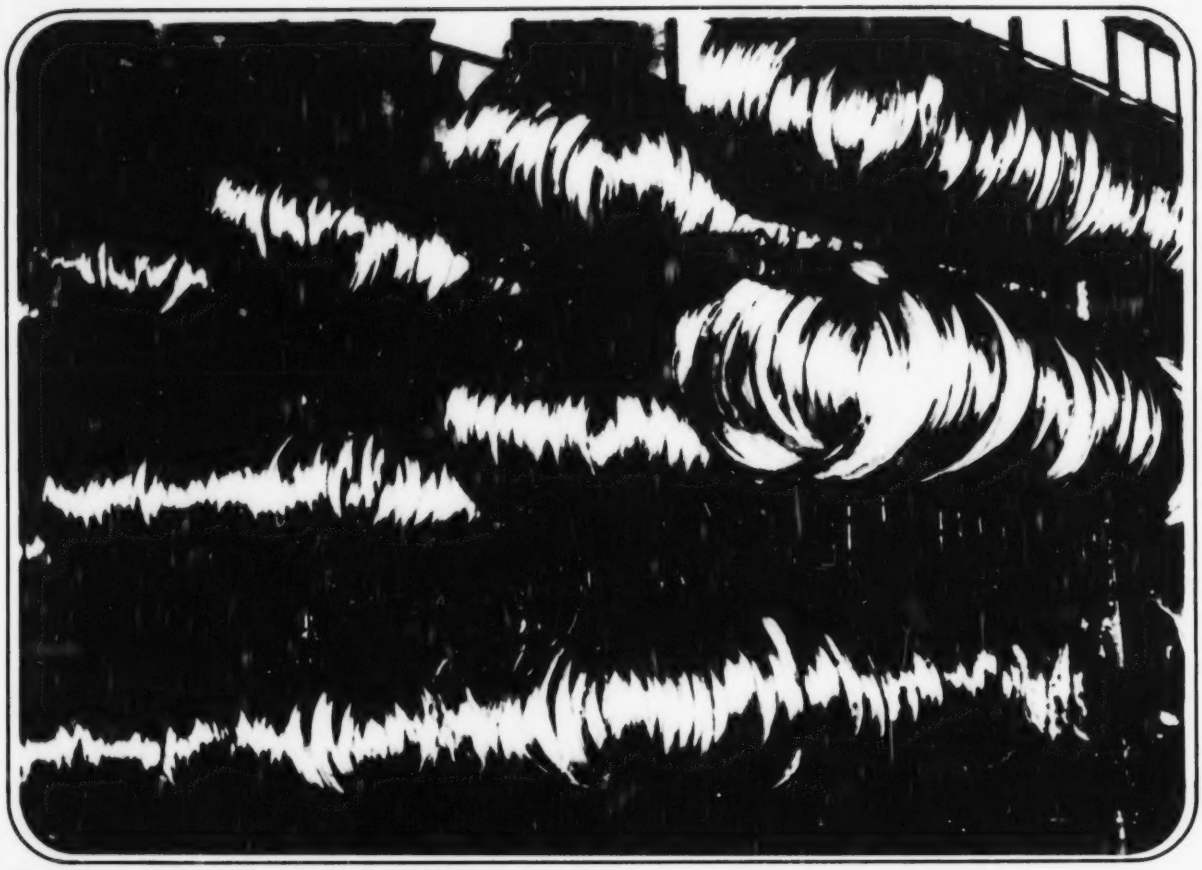


Fine wire following peroxide bright pickling

1. THE SIGNIFICANCE

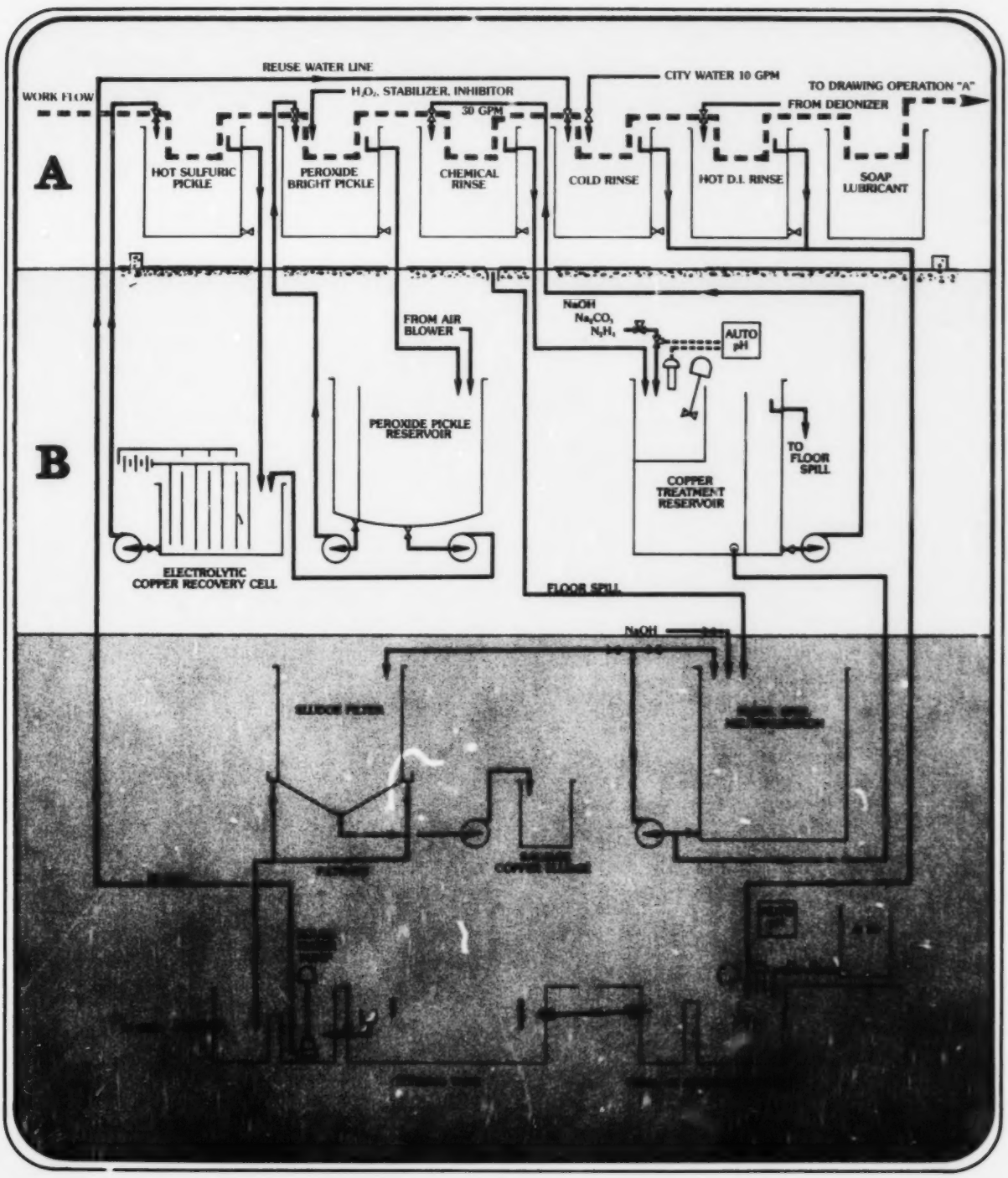
All wire drawing operations require cleaning of the metal surfaces before drawing to prevent surface impurities from being pulled into the drawn wire. This cleaning or "pickling" is usually accomplished by the use of sulfuric or hydrochloric acid. To maintain good pickling activity the solution must be replaced when it reaches a minimum concentration. This depleted pickling solution is then a waste disposal problem.

The metal must also be washed free of pickling solution. The resulting rinse waters contain metal salts. Because of the low concentration of these contaminants the rinses are difficult to treat economically.

In the case of the production of copper wire, additional complications are present because of the chemical reduction of cupric oxide to a cuprous oxide coating which cannot be removed by sulfuric acid. This coating has normally been treated by a "secondary pickle" of chromic acid-sulfuric acid, chromic acid-ammonium bifluoride mixtures, or by nitric acid. All of these techniques produce additional pollutants. Each of the 3 to 4 drawing steps required to produce fine copper wire from copper rod requires these pickling and rinse steps.

The waste from such an operation, if treated by conventional precipitation techniques without an examination of the manufacturing process itself, would impose a severe cost on the manufacturing operation and produce large amounts of sludge for disposal.

In this EPA demonstration grant, the Volco Brass and Copper Company, of Kenilworth, New Jersey, with Lancy Laboratories as consultants, demonstrated that water consumption could be reduced by 90% from 200,000 gallons per day to 20,000 gallons per day by chemical rinsing and water reuse. The sulfuric acid pickle was regenerated and high purity metallic copper recovered by continuous electrolysis, thereby eliminating the dumping of spent pickle liquor. Hydrogen peroxide was proven to be an improved secondary pickle and the chromates and fluorides previously used were eliminated. Total solids leaving the plant in the rinse waters were reduced from 2500 lbs/day to less than 100 lbs/day. Metal losses in the effluent were reduced to less than one pound per day compared to the previous 600-700 pounds per day.


REUSE WATER LINE
CITY WATER 10 GPM
TO DRAWING OPERATION "A"
WORK FLOW
H_2O_2, STABILIZER, INHIBITOR
FROM DEIONIZER
30 GPM
A
HOT SULFURIC PICKLE
PEROXIDE BRIGHT PICKLE
CHEMICAL RINSE
COLD RINSE
HOT D.I. RINSE
SOAP LUBRICANT
B
FROM AIR BLOWER
NaOH
Na_2CO_3
N_2H_4
AUTO pH
PEROXIDE PICKLE RESERVOIR
TO FLOOR SPILL
COPPER TREATMENT RESERVOIR
ELECTROLYTIC COPPER RECOVERY CELL
FLOOR SPILL
NaOH

2. THE NEW PROCESS

The pollution control system which is integrated into the manufacturing process consists of three basic steps:

1. The regeneration and copper recovery system for the primary pickle bath
2. The chemical rinse system
3. The use of hydrogen peroxide plus proprietary additives for the secondary pickle.

Figure 1 illustrates the final process with each section highlighted by separate color.

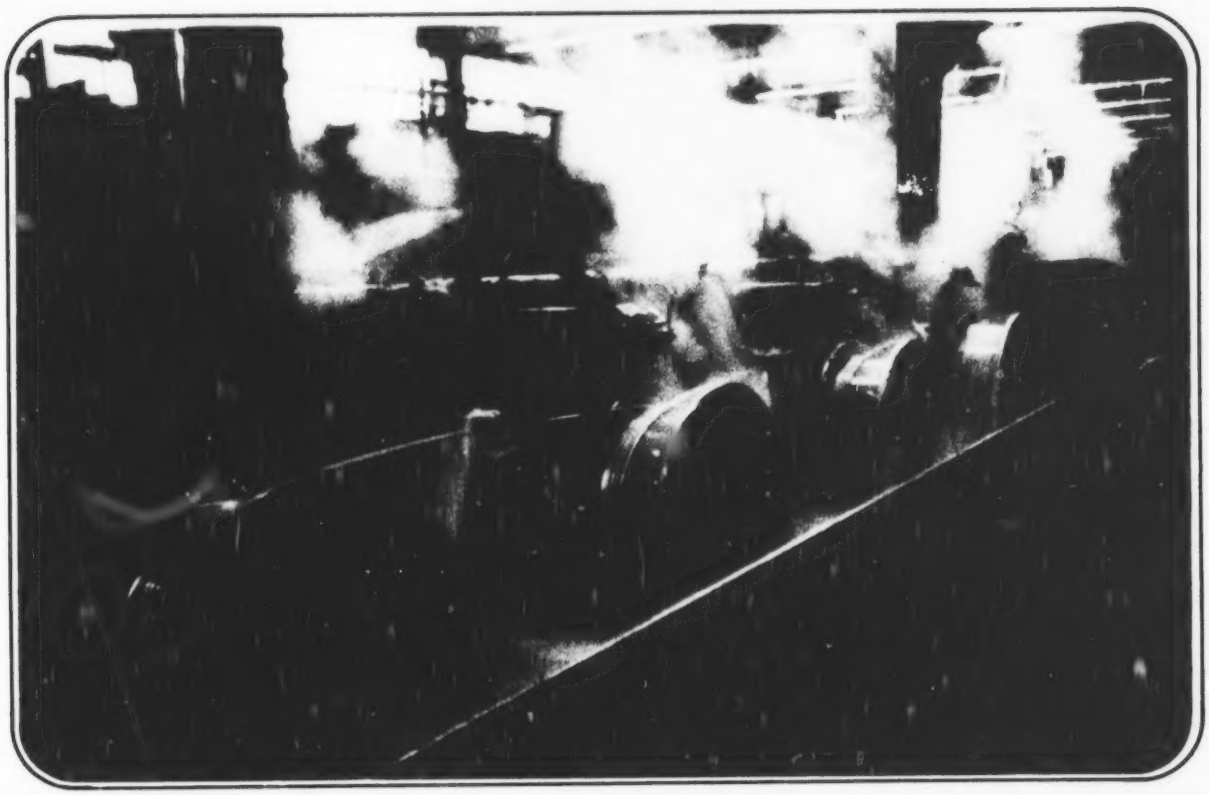
The top block ("A") shows the work flow through the new system. After the hot sulfuric acid pickle and the secondary pickle of 2.5% hydrogen peroxide in sulfuric acid, the work passes through a chemical rinse step which neutralizes the acid drag out. It also precipitates any copper salts by reduction of cupric (Cu^{++}) ions to cuprous (Cu^{+}) ions which are insoluble at the pH of the chemical rinse. The work then goes to a cold rinse using city water, a hot rinse using deionized water, and finally a lubricant bath prior to the drawing operation.

The portion of the flow diagram enclosed as Block "B" shows the electrolytic copper recovery cell, which recovers metallic copper and regenerates sulfuric acid from the metal salts in the hot sulfuric acid pickle solution. It was originally felt that the trace metals (zinc, tin, lead) would interfere with the recovery of pure copper. By controlling current density at five to ten amperes per square foot, however, pure copper can be recovered while maintaining the copper concentration in the pickle bath at fifteen grams per liter.

The secondary pickle reservoir is also shown in Block "B". Copper sulfate accumulates in this bath and eventually crystallizes out. These crystals can be recovered and sold as a copper rich sludge or added to the electrolytic copper recovery loop.

The chemical rinse reservoir is maintained at the proper pH and composition by the addition of caustic, sodium carbonate, and a reducing agent, in this case hydrazine. The sludge draw off along with the flow from the floor spill neutralization first goes to a sludge filter to recover salvage copper sludge and then to a final sump for discharge.

The rinse flows go to a pH adjustment tank, a settling tank and finally to the rinse water sump where the bulk of the flow is recirculated to the first water rinse tank.



Heavy wire drawing

3. THE OLD EFFLUENT VS. THE NEW

PREVIOUS EFFLUENT VS. THE NEW AT VOLCO KENILWORTH NEW JERSEY PLANT

75 TPD of Finished Wire
(Pickled 3-4 Times to obtain Final Product)

lbs/ton finished wire
unless otherwise noted

	OLD	NEW
Water Usage	24000 (150 GPM)	1600 (10 GPM)
pH	3.8	7.5-8.5
Total Cr.	2.2 (90 ppm)	0
Zn	4.8 (200 ppm)	.002 (1 ppm)
Cu	2.4 (100 ppm)	.002 (1 ppm)
Suspended Solids	.7 (30 ppm)	.03 (20 ppm)
Dissolved Solids	36 (1500 ppm)	1.3 (800 ppm)

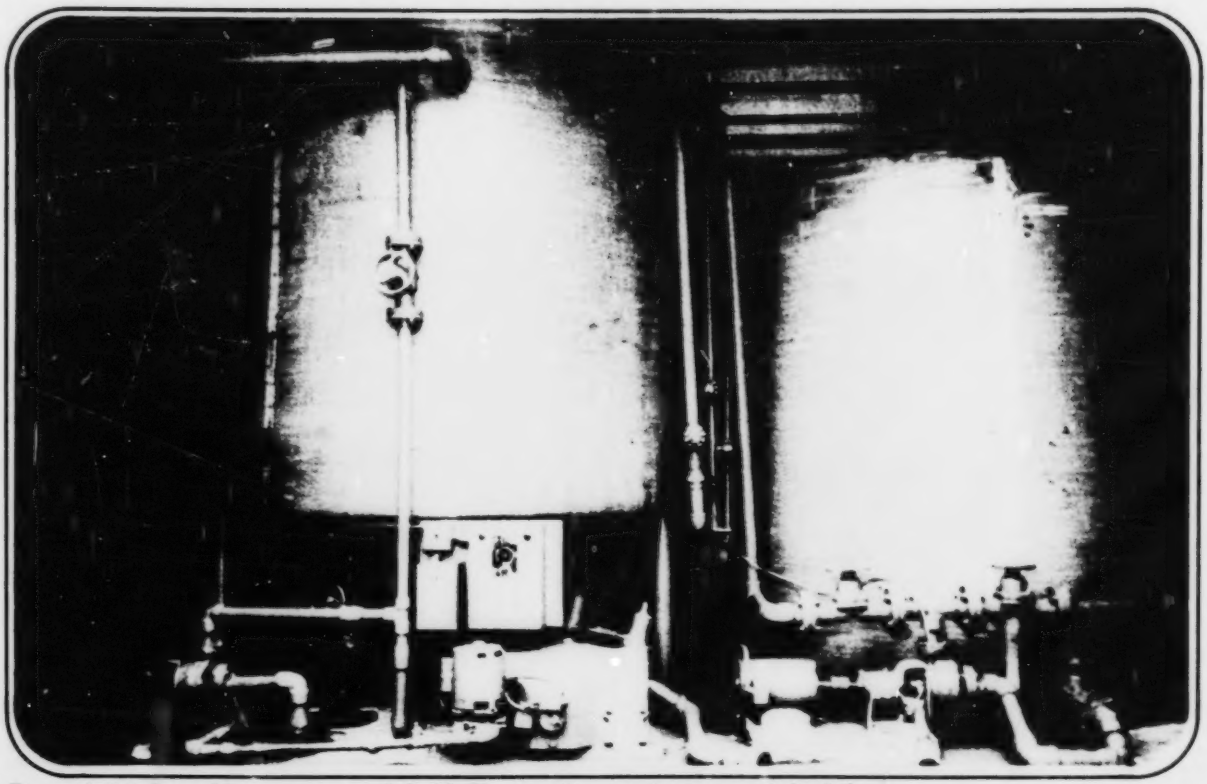
	Previous Operation	Estimate of Cost of Conventional Treatment Without Process Change	Installed Process
TOTAL INVESTMENT	–	$598,000	$141,000
OPERATING COSTS			
I. Wages @ $3.60/hr	$ 1,500	$ 21,600	$ 7,200
II. Utilities & Services			
Power @ 2¢/kw hr.	–	–	600
Sanitary Sewer Charges 150 GPM @ 25¢/m Gal	14,000	14,000	–
Rinse Water @ 25¢/m Gal	14,000	14,000	900
Sludge Haulage @ 8¢/Gal	6,300	6,300	–
III. Maintenance, 3% of Inv.	–	18,000	4,200
IV. Laboratory 2 hr/day @ $3.60/hr	–	1,800	1,800
V. Overhead @ 125% of Oper. & Main. Labor	1,900	32,300	10,400
VI. Raw Materials			
Primary Pickle Chemicals	8,000	8,000	–
Bright Pickle Chemicals	8,100	8,100	36,000
Treatment Chemicals	–	32,000	13,000
TOTAL Materials	16,100	48,100	49,000
TOTAL Operating Costs	53,800	156,100	74,100
Fixed Charges			
Depreciation @ 15 yrs.	–	40,000	9,300
Taxes, Insurance @ .5% of Invest.	–	3,000	700
TOTAL Fixed Charges	–	43,000	10,000
Credits			
Copper at 50¢/lb.	–	–	(10,000)
Sludge at 5½¢/lb.	–	–	(8,000)
Reduced Die Maintenance	–	–	(30,000)
NET YEARLY COST	53,800	199,100	36,100

Total annual cost of pollution abatement system *without* credit for decreased die maintenance $12,300
$.20/ton finished wire

Total annual *profit* of pollution abatement system using Volco staff estimate of decreased die maintenance cost of $30,000 annually = $17,700
$.28/ton finished wire

Estimated annual savings of this pollution abatement program in comparison to waste treatment only = $163,000
$2.61/ton finished wire

4. THE ECONOMICS



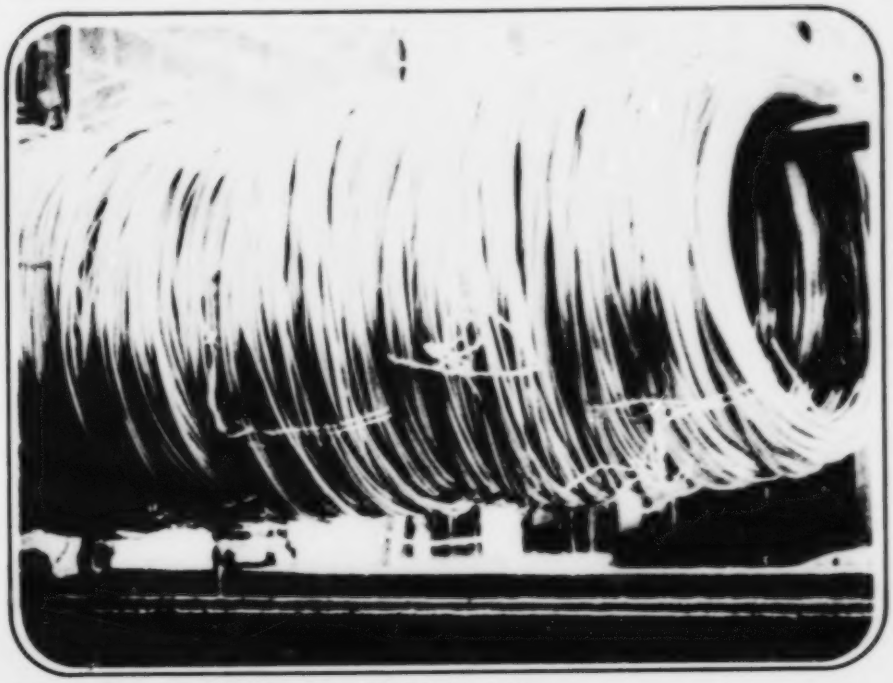
Peroxide bright pickle reservoir tank (left). Floor spill neutralization tank (right).

The economics for this project are presented in comparison to the previous operating situation with essentially no waste treatment, and to estimated costs if a conventional precipitation and neutralization waste treatment system had been installed without modifying the manufacturing process itself. The approach taken for this project gave a major reduction in pollutants, including sludge, at a slight profit, while the isolated installation of a waste treatment system would have resulted in a major cost to the company.

Several changes were made in the plant operation simultaneously with the installation of the pollution abatement system resulting in a total of $100,000 annual savings cost in the drawing operation. The credit of $30,000 annually for increased die life taken for this project is an estimate by the Volco staff.

Electrolytic Copper Recovery Cell

5. AREAS OF APPLICATION



Intermediate wire following peroxide bright pickling

This process is currently being used at five other installations manufacturing copper and copper-alloy products. The chemical rinse technique is applicable to electroplating operations and has gained wide acceptance there. Any facility utilizing a fluoride-chromate bright pickle should consider the use of a hydrogen peroxide-sulfuric acid mixture as an alternative to treatment.

For further information:

Detailed information on this project, is available from the Superintendent of Documents as EPA Report 12010 DPF "Brass Wire Mill Process Changes and Waste Abatement, Recovery and Reuse"

Or write:

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Environmental Protection Agency
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